

V.C.2 Dimensionally Stable High Performance Membrane (SBIR Phase III)

Cortney Mittelsteadt (Primary Contact),
Avni A. Argun, Castro Laicer
Giner, Inc. / Giner Electrochemical Systems (GES), LLC
89 Rumford Avenue
Newton, MA 02466
Phone: (781) 529-0529
Email: cmittelsteadt@ginerinc.com

DOE Manager
HQ: Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov

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determined annually by DOE

and Demonstration Plan. Table 1 lists the DOE's technical targets and where our research and development efforts stand to date.

TABLE 1. DOE Technical Targets and GINER/GES Status

Characteristic	Unit	2017 Target	DSM™ Status
Oxygen crossover	mA/cm ²	2	1.5 ^a
Hydrogen crossover	mA/cm ²	2	1.8 ^a
Membrane Conductivity	S/cm		
Operating Temperature		0.10	0.093 ^b
20°C		0.07	0.083
-20°C		0.01	Not tested
Operating temperature	°C	≤120	95
Area resistance	Ohm*cm ²	0.02	0.03
Cost	\$/m ²	20	~\$100
Lifetime	hours	5,000	Untested
Durability with cycling <80°C	cycles	20,000	20,000
Unassisted start from low temperature	°C	-40	Untested
Thermal cyclability in presence of condensed water		Yes	Yes

^aCrossover measured for 1 atm of *pure H₂ and pure O₂ at 95°C and 50% relative humidity.*

^b*For 18 μm DSM operating at 95°C with H₂/Air at 20 psi. H₂/Air stoichiometry = 1.1/2.0*

Fiscal Year (FY) 2012 Objectives

- Develop a process to fabricate microporous DSM™ support films with 50% pore density.
- Optimize DSM™ support materials to yield high tensile strength and negligible dimensional changes in water at 80°C.
- Qualify the resulting fuel cell membranes by freeze/thaw and wet/dry testing.
- Develop and characterize membrane electrode assemblies (MEAs) based on the DSM™ technology.
- Demonstrate a cost-effective, roll-to-roll adaptable MEA fabrication method.

Technical Barriers

This project addresses the following technical barriers from the 3.4.5 (Fuel Cells)¹ and 3.5.5 (Manufacturing R&D)² sections of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability¹
- (B) Cost¹
- (C) Performance¹
- (A) Lack of High-Volume Membrane Electrode Assembly Processes²

Technical Targets

Progress has been made in achieving the DOE targets listed in the Multi-Year Research, Development

This project is pursuing three DSM™ fabrication processes based on the criteria of performance optimization and cost reduction. As described later in this report, all three processes (ultraviolet microreplication, mechanical deformation, and inversion casting) are based on the use of molding technology and are favorably scalable for high-volume production. Upon completion of their evaluation, the selected process will yield fuel cell membranes that meet the following DOE targets:

- Area resistance: <0.02 Ω.cm²
- Cost: <20 \$/m²
- Lifetime: >5,000 hours
- Durability at 80°C: >20,000 cycles

FY 2012 Accomplishments

- Using a thermal microreplication process, fabricated 4" diameter round high modulus polymer molds with low surface energy to allow rapid release of DSM™ supports. These molds consisted of closely packed vertical pillars with 20 μm diameter and 10 μm height.
- Designed and executed a material matrix that includes a series of photo-crosslinkable polymers such as acrylates,

thiol-enes, epoxies, and urethanes towards selection of a DSM™ support that has high mechanical stability at 80°C in water.

- In collaboration with UMass, utilized a state-of-the-art imprinter to obtain 10- μm -thick thiol-ene DSM™ support with 50% porosity. Demonstrated the versatility of this process by fabricating both standalone and substrate-bound films. Upon incorporation of the ionomer layers, the resulting DSM™ will be $\sim 25\ \mu\text{m}$ thick to yield very low ($<0.02\ \Omega\cdot\text{cm}^2$) area resistance.
- Using a mold-assisted mechanical deformation method, generated highly porous ($\sim 35\%$) polysulfone DSM™ supports at $\$50/\text{m}^2$. This method is projected to yield $<\$20/\text{m}^2$ when adapted to a roll-good process.
- Investigated the phase inversion solvent casting method from Phase II using high-modulus, fluorinated molds to eliminate residual layers.



Introduction

In proton exchange membrane fuel cells, attaining and maintaining high membrane conductivity at various operating conditions is crucial for the fuel cell performance and efficiency. Lowering the equivalent weight (EW) of perfluorinated ionomers is one of the few options available to improve membrane conductivity, especially in the low relative humidity (RH) regime. However, excessive changes in membrane dimensions upon application of wet/dry or freeze/thaw cycles yield catastrophic losses in membrane integrity, hindering their long-term durability. This is especially of concern when low-EW ionomers are used in thin membrane configurations to minimize resistive losses. Incorporating perfluorinated ionomers of low EW within highly porous, dimensionally stable support materials is an optimal method to achieve the DOE membrane metrics for conductivity and durability. A scalable, cost-effective method to fabricate these composite membranes is also necessary to achieve the DOE target of $<\$20/\text{m}^2$. Giner/GES has developed DSM™ technology to provide mechanical support for the conductive ionomer. These composite membranes include a highly conductive and high-acid-content ionomer within a thin and durable polymer support with well-defined pores and high (50%) porosity. Utilizing high-strength engineering polymers, the DSM™ approach has completely restrained in-plane swelling. Providing a non-tortuous, through-plane path for ionic transport minimizes the conductivity penalty due to the support structure. Additionally, when filled with low-EW perfluorinated sulfonic acid (PFSA) ionomers, they meet nearly all of the Department of Energy's 2017 durability and performance targets, including those for freeze/thaw cycling and wet/dry cycling operation.

As currently manufactured, DSM™ is far too expensive ($\sim 1,000/\text{m}^2$) for automotive or even stationary applications. A scalable, continuous fabrication method is needed to reduce the DSM™ cost down to or below the DOE's 2017 cost target of $\$20/\text{m}^2$. This project is directed toward the commercialization of DSM™ for highly reliable fuel cell systems operated under harsh environments. The overall objective of this project is to develop a scaled-up fabrication process geared towards roll-to-roll manufacturing of DSM™.

Approach

A major milestone for this project is to develop a cost-effective route to fabricate a composite DSM™ that includes a low-EW PFSA ionomer embedded in a 10- to 12- μm -thick microporous support film with 20 μm pore diameter and 50% pore density. Currently, three types of micromold-based fabrication techniques are being actively pursued by Giner/GES to achieve the DOE's 2017 targets for cost, performance, and durability. Figure 1 shows scanning electron micrographs of a micromold with 10 μm pillar heights and 50% area coverage that has been generated earlier in the project to utilize the scalability of these micromolding approaches.

"*UV Microreplication*" method is a soft lithography approach that involves the deposition of low-viscosity formulations on a micromold followed by ultraviolet-assisted polymerization to yield highly porous DSM™ substrates. This is a highly scalable process that generates materials at low cost and high volume, and current research is on increasing the mechanical stability of ultraviolet-cured polymers to qualify them as fuel cell components. "*Mechanical Deformation*" method relies on puncturing softened thermoplastics using an array of micropillars. This process is also readily scalable to generate a proven DSM™ support material at low cost, and current research is directed towards the use of fluorinated thermoplastics for effortless release from the micromold. "*Inversion Casting*" method is a solvent-based approach based on the deposition of a solution-processable polymer on a micromold followed by its precipitation using a non-solvent. This process already demonstrated roll-to-roll adaptability in Phase II of this project, and the current research is towards reduction of environmental impact and improvement of mechanical properties. Table 2 ranks each method based on their cost advantages and future prospects as well as the results obtained to date.

Results

UV Microreplication. This process flow involves the use of a low-viscosity, ultraviolet-crosslinkable formulation (precursor) placed between a low-surface-energy mold (Figure 1) and a suitable backing layer such as Nafion® or poly(vinyl alcohol) followed by removal of the crosslinked polymer to yield a DSM™ support with well-defined

TABLE 2. Three DSM™ fabrication techniques compared side-by-side based on several criteria including scalability, materials, and development/final DSM™ cost. (1-Fair, 2-Good, 3- Proven)

Technique	Scalability	Materials	Development cost	Final Cost
UV Microreplication	3	1	1	3
Mechanical Deformation	3	3	2	3
Inversion Casting	2	2	2	2

cylindrical pores. The resulting 10- μm -thick free-standing films have high tensile strength, and they are sufficiently flexible for roll-to-roll adaption. However, they often fail to yield the desired mechanical properties at elevated ($\sim 80^\circ\text{C}$) temperatures. To overcome this issue, Giner/GES prepared and tested a number of polymers to achieve a suitable formulation that will give high tensile strength (>10 MPa), elastic modulus (>100 MPa), and elongation at break ($>5\%$) while retaining dimensional stability and resistance to acid hydrolysis. Table 3 shows a selected list of formulations along with their relevant mechanical properties at 80°C in water. The mechanical properties of a Nafion® 112 film are also given for comparison. Based on the numerous formulations tested to date, a diphenol acrylate polymer (SR348, Sartomer) yielded the most promising properties. Figure 2 shows the chemical structure and stress-strain curves of this polymer in water at 25°C and 80°C as compared to Nafion® 112.

Mechanical Deformation. This is a direct perforation route that involves puncturing softened thermoplastics with tapered micromolds to fabricate porous films. This method can utilize commodity thermoplastics with very fast processing times allowing for roll-to-roll production. Preliminary perforation trials were conducted with polysulfone and yielded 10- to 15- μm -wide pores with less than the targeted 50% porosity as shown in Figure 3. This

TABLE 3. Mechanical Properties of Ultraviolet Crosslinked Polymers Tested at 80°C in Water

Polymer	Family	Tensile Strength (MPa)	Modulus (MPa)	Elongation at Break (%)
Nafion® 112	Perfluoro sulfonic acid	6.08	21.36	3
NOA86 (Norland)	Thiol-enes	0.52	15.5	3.32
EB3300 (Cytec)	Epoxy Acrylate	1.04	48.65	4.97
SR348 (Sartomer)	Phenol Acrylate	9.65	227.1	7.44
EB264 (Cytec)	Urethane Acrylate	2.04	14.07	6.86

was mainly due to excessive tearing of polysulfone during the mold release step. To circumvent this issue, Giner/GES is currently pursuing a high modulus thermoplastic film with high tear-resistance that can be easily released due to the film's low surface energy.

Inversion Casting. First used during Phase II of this project, this method aims to fabricate DSM™ support materials using a solution-processable polymer such as polysulfone. The process involves roll-casting a 30 wt% polysulfone solution from N-methylpyrrolidone on the same polymer micromold shown in Figure 1 followed by rapid precipitation of the polymer in water. Figure 4 shows top-down and cross-sectional views of a 6.8- μm -thick free-standing polysulfone film released from the micromold. It is important to note that the film is free of residual layers to yield the 50% targeted porosity. Since the phase inversion process generates a sponge-like film, it will require further annealing (such as heating above the T_g) to increase the mechanical strength of the films.

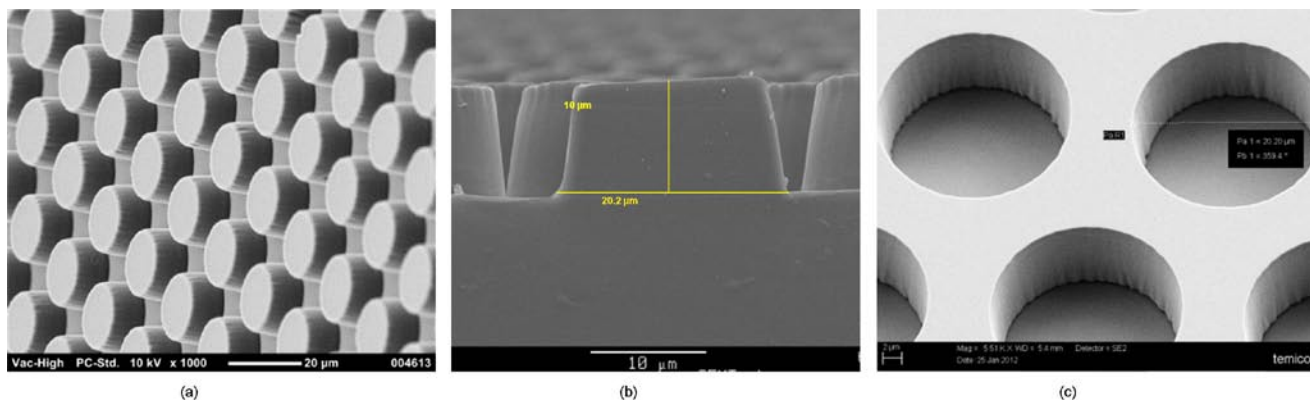


FIGURE 1. Scanning electron micrographs of high modulus, low surface energy polymer micromold pillars (a and b) replicated from an electroplated nickel hole pattern (c)

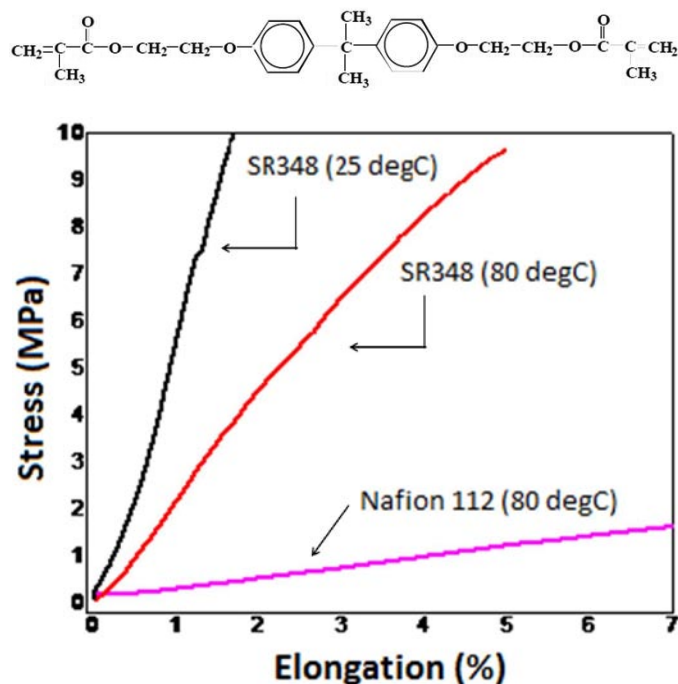


FIGURE 2. Chemical structure of an ethoxylated bisphenol A dimethacrylate polymer (SR348, Sartomer) shown with its stress-strain curves in water at 25°C and 80°C. Also shown is Nafion®’s behavior at 80°C for comparison.

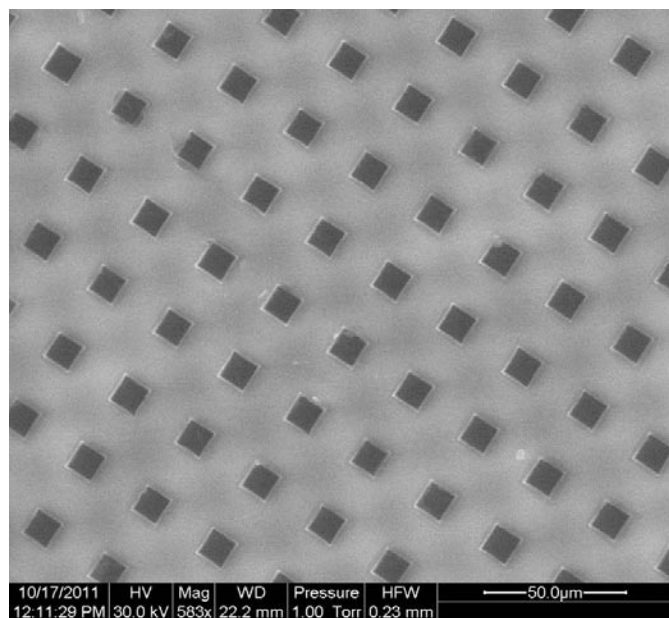


FIGURE 3. Top-down scanning electron micrograph of a perforated polysulfone film with ~30% porosity

Conclusions and Future Directions

The goal by the end of FY 2012 was to demonstrate a scalable process for cost-effective manufacturing of DSMs™

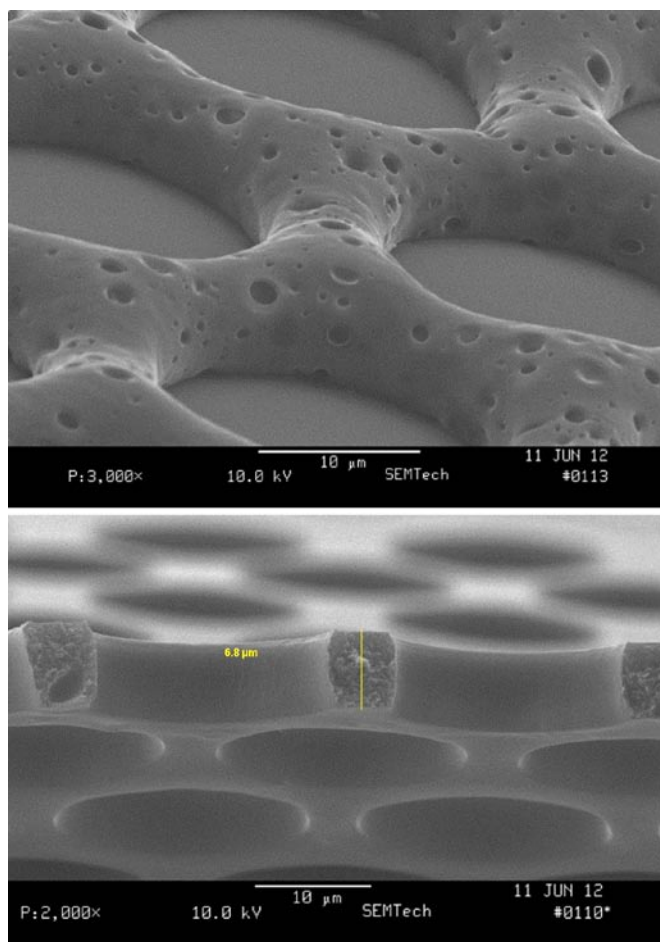


FIGURE 4. Top-down and cross-sectional scanning electron micrographs of a polysulfone film inversion-cast on a micromold from a 30 wt% N-methylpyrrolidone solution

for fuel cells. We believe that we have shown three scalable micromolding methods that are capable of performing this goal. Upon further validation of mechanical properties obtained by the ultraviolet microreplication method, we will start using the roll-to-roll apparatus at University of Massachusetts – Amherst through an ongoing research agreement. The roll-to-roll setup at UMass is specifically tailored for processing of ultraviolet-curable formulations with micromolding (imprint lithography) and will be a valuable asset to the development of this project. The DSM™ supports generated by the mechanical deformation and inversion casting methods will gain traction pending the optimization of process conditions to obtain closely packed micropores to meet the 50% porosity. Their validation as a DSM™ component will be attempted by integrating a low-EW ionomer followed by applying the DSM™ testing protocols that include the measurement of conductivity and freeze-thaw and wet/dry cycling durability.

FY 2012 Publications/Presentations

1. Mittelsteadt, C.K., A. Argun, C. Laicer “4th Quarterly Report” Oct. 2011.
2. Mittelsteadt, C.K., A. Argun, C. Laicer “Annual Progress Report” Dec. 2011
3. Mittelsteadt, C.K., A. Argun, C. Laicer “5th Quarterly Report” Jan. 2012.
4. Mittelsteadt, C.K., A. Argun, C. Laicer “6th Quarterly Report” Apr. 2012.
5. Mittelsteadt, C.K., A. Argun, C. Laicer, J. Willey, P. Maxwell. “2012 Annual Merit Review Proceedings– Fuel Cells ” May, 2012